

Verification and Certification of the  
Translation of

Japanese Patent Application  
Number Hei 11-054834 (54,834/1999)

Applicant: Nihon Parkerizing Company, Limited

Filing Date in Japan: 2 March 1999

by

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## VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare that:

My name and post office address are as stated below;

That I am knowledgeable in the English language and in the language of the

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*(Identification of attached or previously filed document)*

The document for which the attached English translation is being submitted is:

Japanese Patent Application No. Hei 11-054834 filed on 2 March 1999.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true.

Date: 5 May 2000

Full name of the translator Robert L. Meadows

Signature of the translator RL Meadows

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THE STATE OF TEXAS

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§  
§

COUNTY OF TRAVIS

BEFORE ME, THE UNDERSIGNED AUTHORITY, on this day personally appeared

Robert L. Meadows

known to me to be the person whose name is subscribed to the foregoing instrument, and that he signed same for the purpose and consideration therein expressed.

GIVEN UNDER MY HAND AND SEAL OF OFFICE, on this 5th day of May 2000.

Anthony Degollado

Anthony ("Tony") Degollado

Notary Public in and for the State of Texas. Commission expires 31 August 2000.

5 JUNE 2000

Date

(Seal)

# CERTIFICATION

I, Robert L. Meadows, President of

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hereby declare

- (1) that the R. M. Meadows Company is a qualified language translation service registered in Travis County, State of Texas, United States of America;
- (2) that a translator thoroughly familiar with the English and Japanese languages has read the enclosed Japanese-language document; and
- (3) that the appended document is, to the best of our knowledge and belief, an accurate and complete translation, from a copy of the patent application certified as to authenticity (Certification No. 2000-3016946 of 17 March 2000) by the Japanese Patent Office, of:

日本特許出願番号平成11年第054834号.....  
Japanese Patent Application Number Heisei 11-054834.....  
発明の名称: スラッジ発生のないリン酸亜鉛処理液およびリン酸亜鉛処理方法.....  
"surajji hassei no nai rinsan aen shori-eki oyobi rinsan aen shori houhou".....  
"Nonsludging zinc phosphate treatment bath and nonsludging zinc phosphate  
treatment method".....  
Applicant: Nihon Parkerizing Company, Limited.....  
特許出願人: 日本パーカライジング 株式会社.....  
Filed in Japan on 2 March 1999.....

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*Anthony Degollado*

known to me to be the person whose name is subscribed to the foregoing instrument, and acknowledged to me that he is an owner and president of the above-named business and that he signed same for the purpose and consideration therein expressed.

GIVEN UNDER MY HAND AND SEAL OF OFFICE, on this 5th day of June 2000.

*Anthony Degollado*

5 JUNE 2000

Date

Anthony (Tony) Degollado  
Notary Public in and for the State of Texas. Commission expires 31 August 2000.

(Seal)

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## Title of the Invention

Nonsludging zinc phosphate treatment bath  
and nonsludging zinc phosphate treatment method

## Claims

Claim 1. Nonsludging zinc phosphate treatment bath that characteristically comprises an aqueous solution that contains at least phosphoric acid, nitric acid, and zinc wherein the molar concentrations (mol/L) of the  $[H_3PO_4]$ ,  $[HNO_3]$ , and  $[Zn]$  satisfy the following relationship.

$$[Zn] \leq 0.3 [H_3PO_4] + 0.5 [HNO_3]$$

Claim 2. The nonsludging zinc phosphate treatment bath described in Claim 1, that contains as additive at least 1 selection from nitrous acid, permanganic acid, persulfuric acid, hydrogen peroxide, chloric acid, perchloric acid, nitrobenzenesulfonic acid, hydroxylamine, starch/phosphoric acid esters, fluorine compounds, and salts of the preceding.

Claim 3. Nonsludging zinc phosphate treatment method that characteristically comprises cathodic electrolysis treatment of a metal workpiece in a zinc phosphate treatment bath as described in Claim 1 or 2.

Claim 4. The nonsludging zinc phosphate treatment method of Claim 3, in which prior to the aforesaid cathodic electrolysis treatment the metal workpiece is brought into contact with a weakly basic aqueous colloidal solution that contains titanium oxide, titanium hydroxide, and zinc phosphate.

(Detailed Description of the Invention)

(0001)

(Field of the Invention)

This invention relates to a nonsludging zinc phosphate treatment bath and a treatment method that employs this bath. This bath and treatment method are used for the formation of zinc phosphate coatings on metal surfaces.

(0002)

(Description of the Prior Art)

Phosphate treatments are widely used in general as a temporary anticorrosion treatment for iron and steel, as a paint undercoating treatment for iron and steel (including zinc-plated iron and steel) and aluminum, as a lubricant undercoating treatment in the plastic working of iron and steel, and as a lubrication treatment for sliding parts. Phosphate treatments are used for these applications because phosphate coatings, which function as passivating coatings, have the ability to impart corrosion resistance to metals and because these coatings have an excellent affinity for organics (e.g., resins and oils) and as a result support and enable excellent adherence

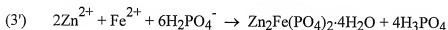
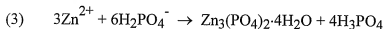
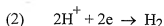
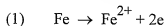
between organics and metal surfaces. In other words, phosphate coatings are equipped with the most essential properties required of a surface treatment coating, i.e., corrosion resistance and adherence.

(0003)

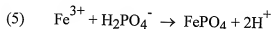
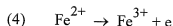
Phosphate coatings occur in a variety of types, such as iron phosphate, zinc phosphate, zinc iron phosphate, zinc calcium phosphate, and manganese phosphate, as a function of the nature of the particular metal workpiece. While each of these coating types is used as appropriate based on its specific properties, the highest demand is for the formation of zinc phosphate coatings and zinc iron phosphate coatings on iron and steel, including zinc-plated iron and steel (composite coatings of zinc phosphate and zinc iron phosphate are usually formed on iron and steel surfaces).

(0004)

The phosphate treatment baths used with iron and steel take the form of acidic aqueous solutions made up from phosphoric acid, nitric acid, and zinc as essential components along with various additives. A conversion coating is formed when, for example, iron or steel is brought into contact with such a bath for several minutes. The elementary reactions in this case can be exemplified as follows.







(0005)

Iron and steel dissolve according to equation (1) in acidic treatment baths such as phosphate treatment baths, and the electrons given up at this point are consumed in the discharge of hydrogen ion as in equation (2), causing an increase in pH at the metal surface. This increase in pH results in a shift in the dissociation equilibrium of the phosphoric acid, resulting in the insolubilization of a portion of the ferrous ion dissolved from the substrate or zinc ion and formation of a coating of zinc phosphate or zinc iron phosphate on the substrate surface according to equation (3) or (3').

(0006)

While the energy source for these coating-forming reactions is dissolution of the substrate according to equation (1), a large fraction of the dissolving ferrous ion ends up unused by the reactions. This "waste" ferrous ion must be removed from the system since it hinders diffusion of the zinc and phosphate ions and thereby lowers the coating-forming reaction rate. In general, the ferrous ion is oxidized to the ferric ion according to equation (4) using an oxidizer additive such as the nitrite ion and precipitates as insoluble iron phosphate according to equation (5).

(0007)

The ability in the case of this chemical reaction system to eliminate the evolved impurities from the system as a solid precipitate enables use of the treatment bath on a semipermanent basis simply by replenishing the consumed components — a feature that has

contributed greatly to the industrial and commercial success of phosphate treatments. This notwithstanding, removal of this hydrous solid (sludge) requires complex management sequences, while the cost of treating the discharged sludge, which is an industrial waste, has been increasing. These factors have recently led to stronger demand specifically for a nonsludging phosphate treatment.

(0008)

The execution of phosphate treatment using cathodic electrolysis is one countermeasure to the sludge problem. Cathodic electrolysis differs from the above-described conversion-based phosphate treatment in that reaction (2) is driven in cathodic electrolysis directly by electrical energy from an outside power source. The substrate dissolution reaction (1) is no longer necessary and the production of iron phosphate sludge can be avoided. However, since sludge actually also contains about 10 to 25% zinc phosphate in addition to iron phosphate, the use of just cathodic electrolysis cannot completely eliminate sludge production.

(0009)

A number of methods for carrying out phosphate treatment by cathodic electrolysis have in fact already been disclosed in the prior art, most prominently in Japanese Laid Open (Kokai or Unexamined) Patent Application Numbers Sho 64-21095 (21,095/1989) and Hei 4-36498 (36,498/1992) and Japanese Laid Open Patent Application (PCT) Number Hei 6-506263 (506,263/1994). The object of Japanese Laid Open (Kokai or Unexamined) Patent Application Number Sho 64-21095 is high corrosion resistance and high adherence in application as a paint undercoating. This method cannot avoid sludge production, however, because the trivalent iron ion is present in its treatment bath. Japanese Laid Open (Kokai or Unexamined) Patent Application Number Hei 4-36498 employs a high zinc-to-phosphoric acid ratio, probably

because its object is the rapid formation of a fine and dense zinc phosphate coating. It is believed that a zinc phosphate sludge will be produced under these conditions. Japanese Laid Open Patent Application (PCT) Number Hei 6-506263, being concerned with countermeasures to the expense and toxicity of the nickel and/or cobalt essential to the performance of phosphate coatings as paint undercoatings, states that the concentration of these species in the treatment bath can be reduced through the use of electrolysis. Thus, no distinctive features can be discerned when the treatment bath compositions used in conversion methods are compared with these teachings; rather fine-sizing and densification (high corrosion resistance) of the coating or rapid coating formation is identified in each case as the advantage to the use of electrolysis and these teachings are silent on the subject of reducing sludge production.

(0010)

(Problems to Be Solved by the Invention)

The prior phosphate treatment technology as described above is thus unable to entirely eliminate sludge production. It is therefore an object of this invention to introduce a zinc phosphate treatment bath that is entirely free of sludge production. Another object of this invention is to introduce a zinc phosphate treatment method that uses said nonsludging zinc phosphate treatment bath.

(0011)

(Means Solving the Problems)

As the result of extensive research directed to solving the problems described above, the inventors discovered that a nonsludging zinc phosphate treatment bath could be

obtained through the specification of the molar concentrations of the phosphoric acid, nitric acid, and zinc in the zinc phosphate treatment bath.

(0012)

More specifically, the nonsludging zinc phosphate treatment bath of this invention characteristically comprises an aqueous solution that contains at least phosphoric acid, nitric acid, and zinc wherein the molar concentrations (mol/L) of the  $[H_3PO_4]$ ,  $[HNO_3]$ , and  $[Zn]$  satisfy the following relationship.

$$[Zn] \leq 0.3 [H_3PO_4] + 0.5 [HNO_3]$$

(0013)

The zinc phosphate treatment bath of this invention preferably also contains as additive at least 1 selection from nitrous acid, permanganic acid, persulfuric acid, hydrogen peroxide, chloric acid, perchloric acid, nitrobenzenesulfonic acid, hydroxylamine, starch/phosphoric acid esters, fluorine compounds, and salts of the preceding.

(0014)

The nonsludging zinc phosphate treatment method of this invention characteristically comprises cathodic electrolysis treatment of a metal workpiece in a zinc phosphate treatment bath according to this invention as described above.

(0015)

In the execution of the nonsludging zinc phosphate treatment method of this invention, the metal workpiece is preferably brought into contact — prior to the aforesaid cathodic electrolysis treatment — with a weakly basic aqueous colloidal solution that contains titanium oxide, titanium hydroxide, and zinc phosphate.

(0016)

The invention will be explained in detail in the following.

Since in general the energy for the reactions in conversion-type phosphate treatment derives from dissolution of the substrate, this energy cannot be externally controlled. In order to bring about occurrence of the coating-forming reactions as rapidly as possible, the treatment composition in this type of treatment is adjusted in such a manner that reaction (3) or (3') will occur immediately upon a small rise in pH at the substrate surface. It is this circumstance that shows that zinc phosphate can precipitate in the bath without even application of a small external excitation to the substrate. It is also the reason for the presence of zinc phosphate in the sludge in real-world situations.

(0017)

In order to avoid this, it is necessary — for given phosphoric acid and nitric acid concentrations — to establish a suitable upper limit for the zinc concentrations that will not induce zinc phosphate precipitation. As the result of experimental investigations into a large number of combinations, the present inventors discovered that this upper zinc concentration limit can be expressed by the following simple empirical relationship at temperatures up to at least 90°C.

$$(6) \quad [\text{Zn}] = 0.3 [\text{H}_3\text{PO}_4] + 0.5 [\text{HNO}_3]$$

[Zn], [H<sub>3</sub>PO<sub>4</sub>], and [HNO<sub>3</sub>] in this equation respectively designate the zinc, phosphoric acid, and nitric acid concentrations in each case in mol/L.

(0018)

Thus, the zinc concentration in zinc phosphate treatment baths encompassed by this invention should not exceed the concentration given by equation (6). As one might readily deduce, such baths would be deemed unsuitable due to their low zinc concentration when viewed from the perspective of prior-art conversion methods. It is for this reason that the zinc phosphate treatment method of this invention requires the application of cathodic electrolysis to the metal workpiece. This feature has two consequences. First, the deficiency in coating-forming activity due to the low zinc concentration is compensated for by electrical energy — an input that is easily controlled from outside the system. Second, by avoiding dissolution of the metal substrate as in equation (1), production of, for example, iron phosphate can be entirely prevented when the metal workpiece is iron or steel.

(0019)

While equation (6) does limit the relationship between the zinc concentration and the phosphoric acid and nitric acid concentrations, it does not specify an absolute value for each of these concentrations. In other words, the observance of equation (6) is sufficient per se for the specific purpose of avoiding sludge production; however, both the phosphoric acid concentration and nitric acid concentration are preferably at least 0.1 mol/L in order to enable zinc phosphate treatment of this invention to deliver appropriate coating weights at industrially practical coating-formation rates. The zinc concentration is for the same reason preferably more than 50% of the upper limit concentration calculated with equation (6). While the upper limit on the phosphoric acid and nitric acid concentrations is not critical, no improvement in the coating-forming activity occurs at a phosphoric acid concentration in excess of 0.6 mol/L or a nitric acid concentration in excess of 1.0 mol/L due to a thickening of the treatment bath. This makes such concentrations

economically undesirable. Furthermore, when in the industrial execution of this invention the absolute value of the phosphoric acid or nitric acid concentration is particularly high and the treatment bath is not adequately stirred, sludge may attach in the heating conduits due to local overheating. In order to avoid this, observance of the following equation in addition to equation (6) is preferred for obtaining higher levels of safety.

$$(7) \quad [\text{Zn}]/[\text{H}_3\text{PO}_4] < 0.91$$

(0020)

A completely nonsludging zinc phosphate treatment can be carried out by immersing the metal workpiece in a zinc phosphate treatment bath as described above and conducting cathodic electrolysis on the workpiece. In regards to the conditions during electrolysis, the amount of applied electricity (current  $\times$  time) should be adjusted in correspondence to the required coating weight, but the use of a current density of 0.5 to 50  $\text{A}/\text{dm}^2$  is preferred in order to obtain a normal coating. While the temperature of the zinc phosphate treatment bath can be in the broad range from 30 to 90°C, the range of 50 to 85°C is preferred based on such considerations as the conductivity of the treatment bath and efficiency of coating formation.

(0021)

The zinc phosphate treatment bath of this invention is subject to the upper limit on the zinc concentration as defined by equation (6) in order to completely prevent sludge production. As stated above, this has the potential for starving deposition of the zinc phosphate

coating, but as long as cathodic electrolysis is employed no problems will arise due to the compensatory capabilities provided by the ability to adjust the current density and amount of applied electricity. With the objectives of microfine-sizing the coating crystals and achieving high coating-formation rates during electrolysis, the inventors have, however, also discovered two tactics for improving the coating formation performance without raising the zinc concentration.

(0022)

One tactic consists of the co-use of additive. In more specific terms, one or more selections from the following is preferably added to the zinc phosphate treatment bath of this invention: nitrous acid, permanganic acid, persulfuric acid, hydrogen peroxide, chloric acid, perchloric acid, nitrobenzenesulfonic acid, hydroxylamine, starch/phosphoric acid esters, fluorine compounds, and salts of the preceding. While these additives are listed in acid form (excluding hydrogen peroxide, hydroxylamine, the starch/phosphoric acid esters, and the fluorine compounds), they may in fact be added directly as the acid or as the alkali metal or ammonium salt. Hydroxylamine is in general preferably added as its salt with, for example, sulfuric acid. Usable as the fluorine compounds are hydrofluoric acid, fluosilicic acid, fluotitanic acid, fluozirconic acid, and so forth; these are preferably added as the acid or alkali metal or ammonium salt. The additive concentration should be selected as appropriate for the required coating formation rate, but in general is preferably in the range from 0.0005 to 0.1 mol/L.

(0023)

The use of additive results in the admixture of ionic species other than those from phosphoric acid, nitric acid, and zinc in the phosphate treatment bath of this invention, which requires some caveats on calculations using equation (6). Equation (6) stipulates the zinc



concentration strictly on the basis of phosphoric acid and nitric acid as "acids". The presence of a cation other than zinc results in neutralization of some portion of the total nitrate ion by this cation component, and this fraction cannot function as an "acid". In contrast, the presence of an anion other than those from phosphoric acid and nitric acid enhances the "acid" activity.

(0024)

Therefore, in calculations with equation (6) using the total nitrate concentration  $[\text{NO}_3^-]$ , the value modified according to equation (8) should be used as the  $[\text{HNO}_3]$  in equation (6) where  $C_1^{p1+}$ ,  $C_2^{p2+}$ , ...,  $C_n^{pn+}$  denote the non-zinc cations present;  $A_1^{q1-}$ ,  $A_2^{q2-}$ , ...,  $A_m^{qm-}$  denote the anions present in addition to those from phosphoric acid and nitric acid;  $[C_1^{p1+}]$ ,  $[C_2^{p2+}]$ , ...,  $[C_n^{pn+}]$  and  $[A_1^{q1-}]$ ,  $[A_2^{q2-}]$ , ...,  $[A_m^{qm-}]$  indicate the molar concentrations (mol/L) of the individual components; and  $p1$ ,  $p2$ , ...,  $pn$  and  $q1$ ,  $q2$ , ...,  $qm$  are the ionic valences of the individual components.

$$(8) \quad [\text{HNO}_3] = [\text{NO}_3^-] - (p1[C_1^{p1+}] + p2[C_2^{p2+}] + \dots + pn[C_n^{pn+}]) + (q1[A_1^{q1-}] + q2[A_2^{q2-}] + \dots + qm[A_m^{qm-}])$$

(0025)

A second tactic for increasing the coating formation performance comprises contacting the metal workpiece — prior to the execution thereon of the zinc phosphate treatment by cathodic electrolysis — with a weakly basic aqueous colloidal solution that contains titanium oxide, titanium hydroxide, and zinc phosphate. The colloidal particles therein adsorb on the

surface of the metal workpiece and function as nuclei for the crystals during ensuing formation of the zinc phosphate coating. The addition of this step not only serves to improve the efficiency of formation of the zinc phosphate coating that is produced by cathodic electrolysis, but also enables extremely fine control of the crystal grain size in the coating. Additional enhancements in advantageous effects can be obtained by combining the first and second tactics.

(0026)

#### Examples

This invention is explained in more specific detail below through working and comparative examples, but is not limited to or by the working examples.

(0027)

#### Example 1

Zinc carbonate ( $\text{ZnCO}_3$ ) was added so as to produce a zinc concentration of 0.5 mol/L to a mixed aqueous solution of phosphoric acid and nitric acid in which the phosphoric acid concentration was 0.4 mol/L and the nitric acid concentration was 0.8 mol/L. When the resulting aqueous solution was heated to 80°C and held at this temperature for 2 hours, absolutely no turbidity was observed in the solution and a transparent appearance was maintained from beginning to end. The zinc concentration in this aqueous solution was lower than the zinc concentration limit of 0.52 mol/L calculated using equation (6).

(0028)

#### Comparative Example 1

Zinc carbonate ( $\text{ZnCO}_3$ ) was added so as to produce a zinc concentration of 0.5 mol/L to a mixed aqueous solution of phosphoric acid and nitric acid in which the phosphoric acid concentration was 0.4 mol/L and the nitric acid concentration was 0.7 mol/L. When the resulting aqueous solution was heated to 80°C and held at this temperature for 2 hours, the gradual development of turbidity was observed and a white precipitate was ultimately produced. The zinc concentration in this aqueous solution was higher than the zinc concentration limit of 0.47 mol/L calculated using equation (6). The white precipitate was filtered off, washed, and dried. X-ray diffraction analysis of the resulting powder identified it as zinc phosphate.

(0029)

#### Example 2

Zinc carbonate ( $\text{ZnCO}_3$ ) was added so as to produce a zinc concentration of 0.65 mol/L to a mixed aqueous solution of phosphoric acid and nitric acid in which the phosphoric acid concentration was 0.6 mol/L and the nitric acid concentration was 1.0 mol/L. When the resulting aqueous solution was heated to 80°C and held at this temperature for 2 hours, absolutely no turbidity was observed in the solution and a transparent appearance was maintained from beginning to end. The zinc concentration in this aqueous solution was lower than the zinc concentration limit of 0.68 mol/L calculated using equation (6).

(0030)

#### Comparative Example 2

Zinc carbonate ( $\text{ZnCO}_3$ ) was added so as to produce a zinc concentration of 0.65 mol/L to a mixed aqueous solution of phosphoric acid and nitric acid in which the phosphoric acid concentration was 0.6 mol/L and the nitric acid concentration was 0.9 mol/L. When the resulting aqueous solution was heated to 80°C and held at this temperature for 2 hours, the gradual development of turbidity was observed and a white precipitate was ultimately produced. The zinc concentration in this aqueous solution was higher than the zinc concentration limit of 0.63 mol/L calculated using equation (6).

(0031)

### Example 3

Zinc carbonate ( $\text{ZnCO}_3$ ) was added so as to produce a zinc concentration of 0.25 mol/L to a mixed aqueous solution of phosphoric acid and nitric acid in which the phosphoric acid concentration was 0.2 mol/L and the nitric acid concentration was 0.4 mol/L. When the resulting aqueous solution was heated to 80°C and held at this temperature for 2 hours, absolutely no turbidity was observed in the solution and a transparent appearance was maintained from beginning to end. The zinc concentration in this aqueous solution was lower than the zinc concentration limit of 0.26 mol/L calculated using equation (6).

(0032)

### Comparative Example 3

Zinc carbonate ( $\text{ZnCO}_3$ ) was added so as to produce a zinc concentration of 0.3 mol/L to a mixed aqueous solution of phosphoric acid and nitric acid in which the phosphoric

acid concentration was 0.2 mol/L and the nitric acid concentration was 0.4 mol/L. When the resulting aqueous solution was heated to 80°C and held at this temperature for 2 hours, the gradual development of turbidity was observed and a white precipitate was ultimately produced. The zinc concentration in this aqueous solution was higher than the zinc concentration limit of 0.26 mol/L calculated using equation (6).

(0033)

#### Example 4

Hot-rolled JIS S45C was degreased and then dipped for 30 seconds in 5% HCl at ambient temperature to prepare a test panel whose surface was freed of its oxide film. This test panel was then dipped in the aqueous solution of Example 1 heated to 80°C and subjected to cathodic electrolysis at a current density of  $10 \text{ A/dm}^2$ . A zinc phosphate coating was thereby formed on the surface of the test panel. Investigation of the electrolysis time that produced a 50% surface coverage ratio by the zinc phosphate coating gave a value of 10 seconds. The coverage ratio was determined by SEM observation at 500X. At this time point the crystal size in the zinc phosphate coating was a maximum of approximately 50  $\mu\text{m}$ . Zinc phosphate treatment was also carried out by electrolysis under the same conditions (current density =  $10 \text{ A/dm}^2$ , electrolysis time = 10 seconds) with the addition of 0.001 mol/L sodium nitrite ( $\text{NaNO}_2$ ) to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating had improved to approximately 90%. In this case the crystal size in the zinc phosphate coating was a maximum of approximately 40  $\mu\text{m}$ .

(0034)

### Example 5

Zinc phosphate treatment was carried out by electrolysis under entirely the same conditions as in Example 4 (current density =  $10 \text{ A/dm}^2$ , electrolysis time = 10 seconds) with the addition of 0.007 mol/L sodium fluoride (NaF) and 0.04 mol/L fluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating was 100%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately 30  $\mu\text{m}$ .

(0035)

### Example 6

Zinc phosphate treatment was carried out by electrolysis under entirely the same conditions as in Example 4 (current density =  $10 \text{ A/dm}^2$ , electrolysis time = 10 seconds) with the addition of 0.001 mol/L potassium permanganate ( $\text{KMnO}_4$ ) to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating was 100%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately 60  $\mu\text{m}$ .

(0036)

### Example 7

Zinc phosphate treatment was carried out by electrolysis under entirely the same conditions as in Example 4 (current density =  $10 \text{ A/dm}^2$ , electrolysis time = 10 seconds) with the

addition of 0.01 mol/L sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating was 100%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately 30  $\mu\text{m}$ .

(0037)

#### Example 8

Zinc phosphate treatment was carried out by electrolysis under entirely the same conditions as in Example 4 (current density = 10  $\text{A}/\text{dm}^2$ , electrolysis time = 10 seconds) with the addition of 0.005 mol/L sodium meta-nitrobenzenesulfonate ( $\text{C}_6\text{H}_4\text{NO}_2\text{SO}_3\text{Na}$ ) to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating was 100%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately 40  $\mu\text{m}$ .

(0038)

#### Example 9

Zinc phosphate treatment was carried out by electrolysis under entirely the same conditions as in Example 4 (current density = 10  $\text{A}/\text{dm}^2$ , electrolysis time = 10 seconds) with the addition of 0.01 mol/L hydroxylamine sulfate ( $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$ ) to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating was 85%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately 60  $\mu\text{m}$ .

(0039)

### Example 10

Zinc phosphate treatment was carried out by electrolysis under entirely the same conditions as in Example 4 (current density =  $10 \text{ A/dm}^2$ , electrolysis time = 10 seconds) with the addition of 2 g/L sodium starch phosphate ester to the Example 1 aqueous solution. SEM observation showed that the coverage ratio by the coating was 100%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately  $60 \mu\text{m}$ .

(0040)

### Example 11

A JIS S45C test panel was first degreased and acid rinsed and was thereafter dipped for 30 seconds at ambient temperature in a 3 g/L aqueous solution of PREPALENE® Z (colloidal titanium solution), a surface conditioner from Nihon Parkerizing Co., Ltd. The test panel was then immediately subjected to zinc phosphate treatment by electrolysis under entirely the same conditions as in Example 4 (current density =  $10 \text{ A/dm}^2$ , electrolysis time = 10 seconds) using the aqueous solution described for Example 1. SEM observation showed that the coverage ratio by the coating was 100%. At this point the crystal size in the zinc phosphate coating was a maximum of approximately  $15 \mu\text{m}$ .

(0041)

The treatment bath remained transparent from beginning to end in each of the cathodic electrolysis steps in Examples 4 to 11, and in each case the production of a precipitate was also entirely absent.



(0042)

Examples 1 to 3 demonstrate that no precipitation of zinc phosphate occurred even when a zinc phosphate treatment bath of this invention, i.e., a bath containing a zinc concentration less than or equal to the zinc concentration limit defined by equation (6), was heated to 80°C. In contrast to this, as shown in Comparative Examples 1 to 3, precipitation of zinc phosphate did occur in the case of zinc phosphate treatment baths containing a zinc concentration in excess of the zinc concentration limit defined by equation (6).

(0043)

As demonstrated by Examples 4 to 10, the use of additive-containing zinc phosphate treatment baths according to this invention enabled the formation of zinc phosphate coatings at excellent coverage ratios even in relatively short electrolysis time, e.g., 10 seconds.

(0044)

Finally, as demonstrated by Example 11, application of the colloidal titanium surface conditioning treatment of this invention prior to the electrolytic zinc phosphate treatment not only resulted in the formation of a coating with a perfect coverage ratio, but also supported the formation of a coating that contained extremely fine and dense zinc phosphate crystals.

(0045)

#### (Advantageous Effects of the Invention)

Use of the zinc phosphate treatment bath of this invention completely eliminates the production of industrial waste (sludge) that has plagued the prior art and in this manner makes a substantial contribution to reducing global environmental pollution. The method of this invention enables zinc phosphate treatment to be run very rapidly through the use of electrolysis.

This feature, in combination with the fact that this method can be used to execute zinc phosphate treatment on essentially any material that is electrically conductive, makes the instant method highly advantageous on an industrial or commercial basis.

(Document Designation)      Abstract

(Abstract)

(Problem)

To provide a nonsludging zinc phosphate treatment bath and a nonsludging zinc phosphate treatment method.

(Solution)

A zinc phosphate treatment bath in which the molar concentrations  $[Zn]$ ,  $[HNO_3]$ , and  $[H_3PO_4]$  of the Zn,  $HNO_3$ , and  $H_3PO_4$  satisfy the following equation:  $[Zn] \leq 0.3 [H_3PO_4] + 0.5 [HNO_3]$ . In a preferred embodiment, this zinc phosphate treatment bath contains as additive at least 1 selection from nitrous acid, permanganic acid, persulfuric acid, hydrogen peroxide, chloric acid, perchloric acid, nitrobenzenesulfonic acid, hydroxylamine, starch/phosphoric acid esters, fluorine compounds, and salts of the preceding. According to this invention, cathodic electrolysis is executed on the metal workpiece in the aforesaid zinc phosphate treatment bath. Alternatively, the metal workpiece is subjected to cathodic electrolysis in the aforesaid zinc phosphate treatment bath after the workpiece has been brought into contact with a weakly basic aqueous colloidal solution that contains titanium oxide, titanium hydroxide, and zinc phosphate.

(Selected Drawing(s))      None

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